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(71)Applicant : **NGK SPARK PLUG CO LTD**

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(72)Inventor : **SUGIMOTO MAKOTO**
MASUDA KOUMEI

(30)Priority

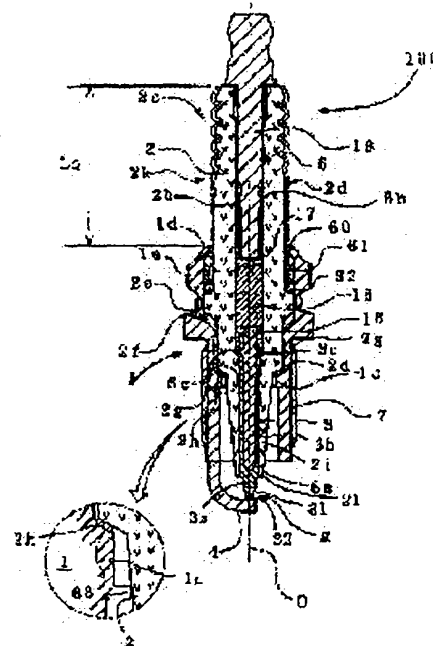
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(54) SPARK PLUG AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a spark plug for which its insulator is covered with a glazed layer that can be glazed at a relatively low temperature and has a high insulating property.

SOLUTION: In this spark plug 100 having a resistor, its glazed layer 2d formed on the surface of an alumina-based insulator 2 has a composition containing 18-35 wt.% of SiO₂, 25-40 wt.% of B₂O₃, 10-25 wt.% of ZnO, 7-20 wt.% of BaO, 3-9 wt.% of Na₂O, and 3-9 wt.% of K₂O. This glaze hardly causes a crack or the like because the difference between its linear expansion coefficient and that of the alumina-based insulating material is relatively small. In addition, it has a softening temperature lower than that of conventional lead silicate glass, so that the glazing temperature can be lowered to 800-950°C, and oxidation in a central electrode 3 or a terminal metal fitting 13 hardly occurs even when the glazing is carried out simultaneously with a glass sealing process. Although its content of the alkaline metal



constituent is high, it has a good insulating property and is excellent in flashover resistance.

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to a spark plug and its manufacture method.

[0002]

[Description of the Prior Art] The spark plug used for ignition of internal combustion engines, such as an automobile engine, has the structure where the insulator which consisted of alumina system ceramics etc. has been arranged, and the center electrode has generally been arranged inside the insulator inside the subject metallic ornaments by which a grounding electrode is attached. It projects from back side opening of subject metallic ornaments to shaft orientations, terminal metallic ornaments are arranged inside the lobe, and an insulator is connected with a center electrode through a conductive glass-seal layer, a resistor, etc. in which this is formed of a glass-seal process. And spark discharge will arise about the gap formed between the grounding electrode and the center electrode by impressing high pressure through the terminal metallic ornaments.

[0003] However, when the conditions of plug temperature becoming high or surrounding humidity rising lap, the so-called flashover phenomenon which does not carry out a leaping flame to a gap even if it carries out high-pressure impression, but discharges between terminal metallic ornaments and subject metallic ornaments in the form which turns around the front face of an insulator lobe may arise. Therefore, in almost all the spark plugs currently generally used, the cover coat layer is mainly formed in the insulating body surface for this flashover phenomenon prevention. On the other hand, a cover coat layer smooths an insulating body surface, and contamination is prevented or it also plays chemical or the role of raising a mechanical strength.

[0004]

[Problem(s) to be Solved by the Invention] Formation of the cover coat layer to an insulator applies a cover coat slurry to an insulating body surface, and is performed by what (called "glost firing") this is calcinated for. Since a cover coat layer is formed by afterbaking attachment at the glost firing temperature of 1000-1100 degrees C to an insulator [finishing / baking] in the case of the alumina system insulator for spark plugs, the cover coat of the lead silicate glass system in which comparatively a lot of PbO(s) were blended with silicate glass, and the softening temperature was reduced is used conventionally. However, this has the following faults. ** As compared with the alumina system insulating material used as a ground, coefficient of linear expansion is small, and it is easy to produce a cracking crack etc. in the cover coat layer obtained. ** In spite of carrying out considerable-amount combination of the PbO, glost firing temperature is still as high as 1000 degrees C or more. In the manufacturing process of a spark plug, although glost firing is also simultaneously performed in many cases at the time of a glass-seal process for man day curtailment, when glost firing temperature is high as mentioned above, there is a difficulty that oxidization of terminal metallic ornaments or a center electrode becomes easy to progress. In addition, since glost firing temperature is reduced further, although it is possible to blend alkali-metal oxides, such as Na₂O, if the content of the alkali-metal component in a cover coat increases too much, an insulating fall will be caused, and there is a problem which becomes easy to produce a flashover. ** In the recent years when the interest about environmental protection is increasing on a scale of the earth, the cover coat containing Pb is kept at arm's length increasingly gradually. For example, examination by use of the spark plug for which the spark plug used Pb content cover coat in consideration of the influence on the environment by the abandonment spark plug in the auto industry used so much being abolished in the future is also advanced.

[0005] It is in the first of the technical problem of this invention offering the spark plug from which insulation also formed the high cover coat layer on the insulator possible [glost firing] at low temperature as compared with the conventional cover coat, and its manufacture method. Moreover, the second of a technical problem is to offer the spark plug which also suited the movement to environmental protection can cut down sharply the amount of content Pb(s) in a cover coat, as a result increasing.

[0006]

[Means for Solving the Problem and its Function and Effect] The first composition of the spark plug of this invention has a center electrode, the subject metallic ornaments arranged on the outside of the center electrode, the grounding electrode arranged so that an end may be combined with the subject metallic ornaments and it may counter with a center electrode, the insulator arranged so that the outside of a center

electrode may be covered between a center electrode and subject metallic ornaments, and the cover coat layer formed with a wrap gestalt in a part of front face [at least] of the insulator. In order to solve the above-mentioned technical problem, an oxidized element component mainly And Si, B, Zn, and Ba, [the cover coat which constitutes this cover coat layer] It consists of two sorts (two sorts of these components are hereafter called ***** alkali-metal component) chosen from Na, K, and Li. B component to B-2 O3 18 to 35% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the Si component SiO2 25 - 40 % of the weight, While containing Ba component seven to 20% of the weight in BaO ten to 25% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the Zn component at ZnO the above -- an addition alkali-metal component -- Na -- Na2O and K2O and Li are characterized by containing three to 9% of the weight in Li2O by the weight which carried out oxide conversion, respectively

[0007] Since the difference of coefficient of linear expansion with this is comparatively small when the insulator of a ground consists of for example, alumina system insulating materials, a cracking crack etc. cannot produce easily the cover coat of the notation composition used for the first composition of the above in the cover coat layer obtained. Moreover, from the content of an alkali-metal component being set up comparatively more highly, rather than the cover coat of the conventional lead silicate glass system, a softening temperature is low and can carry out [low temperature]-izing of the glost firing temperature with 800-950 degrees C. Therefore, when performing glost firing simultaneously with the above-mentioned glass-seal process, it is hard to produce oxidization to a center electrode, the terminal metallic ornaments mentioned later.

[0008] Moreover, insulation is good although the content of an alkali-metal component is high. The point of ***** (ing) two kinds which do not carry out independent addition of one kind of alkali-metal component about this, but are chosen from Na, K, and Li is important. That is, when an alkali-metal component is blended independently according to examination of this invention person, it turns out that the conductivity of a cover coat increases rapidly with increase of the content, the conductivity of a cover coat does not increase so much even if the sum total content increases considerably also unexpectedly, but good insulation can be secured if it blends combining two kinds of things although it leads to insulation being spoiled remarkably. Consequently, the content of an alkali-metal component can be increased without reducing insulation so much, and it becomes possible to attain simultaneously two purposes of low-temperature-izing of reservation of flashover-proof nature, and glost firing temperature as a result. In addition, it is also possible to blend other alkali-metal components after the third component in the range by which the effect of the conductive suppression by ***** of an alkali-metal component is not spoiled

[0009] Si component content in a cover coat is set as SiO2 to 18 - 35% of the weight by the weight which carried out oxide conversion. If this Si component content becomes less than 18% of the weight when the insulator of a ground consists of alumina system insulating materials, the coefficient of linear expansion of a cover coat will become large too much, and it will become easy to produce defects, such as a cracking crack, in a cover coat layer. On the other hand, if this Si component content exceeds 40 % of the weight, the coefficient of linear expansion of a cover coat will become small too much conversely, and it will become easy to produce defects, such as intrusion (crazing), in a cover coat layer. In addition, as for this Si component content, it is good to set up in 25 - 30% of the weight of the range desirably.

[0010] Moreover, B component content is set as B-2 O3 to 25 - 40% of the weight by the weight which carried out oxide conversion. If this B component content will be less than 25% of the weight, the softening temperature of a cover coat may rise and the glost firing in expected temperature (the above-mentioned 800-950 degrees C) may become impossible. On the other hand, if B component content exceeds 40 % of the weight, it becomes easy to produce phase splitting in the cover coat layer obtained, and a cover coat layer may devitrify or it may be connected with problems, such as an insulating fall or coefficient-of-linear-expansion nonconformance with a ground. In addition, as for this B component content, it is good to set up in 30 - 35% of the weight of the range desirably.

[0011] Zn component content is set as ZnO in 10 - 25% of the weight of the range by the weight which carried out oxide conversion. If this Zn component content will be less than 10% of the weight, the softening temperature of a cover coat may rise and the glost firing in expected temperature may become impossible. On the other hand, if this Zn component content exceeds 25 % of the weight, the coefficient of linear expansion of a cover coat will become large too much, and it will become easy to produce defects, such as a cracking crack, in a cover coat layer. In addition, as for the content of this Zn component, it is good to set up in 12 - 18% of the weight of the range desirably.

[0012] Moreover, Ba component content is set as BaO in 7 - 20% of the weight of the range by the weight which carried out oxide conversion. If Ba component content will be less than 7% of the weight, the insulation of a cover coat may fall and it may lead to flashover-proof nature being spoiled. On the other hand, if Ba component content exceeds 20 % of the weight, the softening temperature of a cover coat may rise and the glost firing in expected temperature may become impossible. In addition, as for the content of this Ba component, it is good to set up in 8 - 15% of the weight of the range desirably.

[0013] next -- the ***** alkali-metal component in a cover coat -- Na -- Na₂O and K₂O -- two of sorts of they contain O and Li three to 9% of the weight in Li₂O by the weight which carried out oxide conversion, respectively If the content of one of components will be less than 3% of the weight at least, the softening temperature of a cover coat may rise and the glost firing in expected temperature may become impossible. Moreover, if the content of one of components exceeds 9 % of the weight at least, the coefficient of linear expansion of a cover coat will become large too much, and it will become easy to produce defects, such as a cracking crack, in a cover coat layer.

[0014] Moreover, as for the sum total content of the ***** alkali-metal component in a cover coat, it is good to adjust in 6 - 14% of the weight of the range by oxide conversion. If the sum total content of a ***** alkali-metal component will be less than 6% of the weight, the softening temperature of a cover coat may rise, and the glost firing in expected temperature may become impossible. On the other hand, if this sum total content exceeds 14 % of the weight, the insulation of a cover coat falls and flashover-proof nature may be spoiled.

[0015] furthermore, Na among two sorts of components which make the ***** alkali-metal component in a cover coat -- Na₂O and K₂O -- when oxide conversion are carried out at Li₂O, respectively, as for O and Li, it is good to adjust the value of A1/A2 when setting A1 and the mol content of the thing of another side to A2 for the mol content of the thing of one of these in 1.0-2.0 If the value of A1/A2 separates from this range to a top or the down side, the effect of the conductive suppression by ***** of an alkali-metal component cannot be attained enough, as a result the insulation of a cover coat falls, and flashover-proof nature may be spoiled. In addition, as for the value of A1/A2, adjusting in 1.5-2.0 desirably is good.

[0016] In addition, in order to suppress conductive elevation of the cover coat accompanying the increase in an alkali-metal component content, it divides and is desirable as a ***** alkali-metal component to use two sorts, Na and K. In this case, it is good to make K₂O contain K component three to 9% of the weight three to 9% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the Na component at Na₂O.

[0017] Moreover, as for the sum total content in the value in which the cation component in a cover coat, i.e., Si component, B component, Zn component, Ba component, and the ***** alkali-metal component carried out each oxide conversion, it is desirable that it is 95 % of the weight or more. If these sum total contents will be less than 95% of the weight, the softening temperature of a cover coat may rise, and the glost firing in expected temperature may become impossible. In addition, as for this sum total content, it is good that it is 97% of the weight or more desirably.

[0018] To a cover coat, as an auxiliary cation component, next, aluminum, calcium, Fe, Zr, One sort of Ti, Sr, Mg, Bi, nickel, Sn, P, and Mn, or two sorts or more aluminum -- aluminum 2O₃ -- calcium to CaO Zr for Fe ZrO₂ at Fe 2O₃ Ti -- TiO₂ -- Sr -- SrO -- Mg -- MgO -- Bi can make NiO contain nickel in 5 or less % of the weight of the range in total in Bi 2O₃ by the weight in which Sn carried out PP2O₅ SnO₂, and Mn carried out oxide conversion at MnO, respectively According to the various purposes, it can also add positively, and these components may be mixed impossibly as an impurity (or contamination) from a raw material (or clay mineral blended at the time of manufacture of the cover coat slurry mentioned later), the refractory material in a melting process, etc. In addition, as a source of Fe component in the raw material of a cover coat, although all of the thing (for example, FeO) of Fe(II) ion system and the thing (for example, Fe 2O₃) of Fe (III) ion system are usable, the content of Fe component in a final cover coat layer shall be displayed with the value converted into Fe 2O₃ regardless of Fe valence of ion.

[0019] When the sum total content of the above-mentioned auxiliary cation component exceeds 5 % of the weight, it becomes impossible to secure 95 % of the weight or more of sum total contents of the main cation component. As for the sum total content of an auxiliary cation component, it is good to consider as 3.0 or less % of the weight desirably. In addition, in the following explanation, when naming generically the main cation component and an auxiliary cation component, it may only be described as a cation component.

[0020] For example, aluminum component can acquire the effect which suppresses devitrification of a cover coat by blending in 5 or less % of the weight of the range. Moreover, other components can be

suitably blended, in order to adjust the softening temperature of a cover coat. Especially combination of Bi₂O₃ is effective when lowering the softening temperature of a cover coat.

[0021] Moreover, even if a cover coat does not contain Pb component substantially or (however, what is mixed unescapable is removed from a cover coat raw material etc.) contains it, the content can make it 1.0 or less % of the weight of a thing by PbO conversion. For example, if Pb component contains in the form of the low ion (for example, Pb²⁺) of a valence in the cover coat, this oxidizes to ion with a high valence (for example, Pb³⁺) by the corona discharge from a cover coat layer front face etc., the insulation of a cover coat layer falls, and flashover-proof nature may be spoiled. On the other hand, since the interest about environmental protection is increasing recently, it gropes for the material of a unleaded system also about the cover coat. Since the point and the cover coat used for the spark plug of this invention will not produce a problem at all even if it reduces Pb even on the level which is not contained substantially if the thing to about 1.0 % of the weight contained, for example as an unescapable impurity from the aforementioned cation component not containing Pb component is removed, it can be said that it is convenient. That is, the second technical problem of this invention is solved. In addition, as for the content of Pb, it is good to consider as 0.1 or less % of the weight desirably.

[0022] Next, the important section except a cover coat layer of the second composition of the spark plug of this invention is the same as that of said first composition. The cover coat which constitutes a cover coat layer And the subjects Si, B, Zn, and Ba of a cation component (henceforth the main cation component), Consist of at least one sort chosen from Ti and Zr, and Si component to SiO₂ by the weight which carried out oxide conversion 20 - 40 % of the weight, While containing Ba component ten to 23% of the weight in BaO 15 to 25% of the weight by the weight which carried out oxide conversion 20 to 35% of the weight with the weight which carried out the oxide conversion of the Zn component at ZnO in the weight which carried out the oxide conversion of the B component at B₂O₃ Ti and Zr use as an alkali-metal component at least one sort which contains two to 10% of the weight in total by the weight in which carried out Ti TiO₂ and Zr carried out oxide conversion ZrO₂, respectively, and is chosen from Na, K, and Li. Na -- Na₂O and K -- K₂ -- it is characterized by for O and Li having made the sum total content 12 or less % of the weight by the weight which carried out oxide conversion at Li₂O, and making the content of Pb into 0.1 or less % of the weight further in the form which carried out oxide conversion at PbO

[0023] This second composition includes the following four invention corresponding to the claims 8-11 indicated on the specifications of the time of application. These four invention can also be carried out combining two or more arbitrary things.

(The first invention) Si component is made into 20 - 38 % of the weight by the weight which carried out oxide conversion SiO₂ (the second - the fourth invention -- either and combination are possible at least)

(The second invention) ZrO₂ equivalent-weight content of Zr is made into 3.4 or less % of the weight (the first and the third and fourth invention -- either and combination are possible at least)

(The third invention) TiO₂ equivalent-weight content of Ti is made into 1.5 % of the weight or more (the first and the second and fourth invention -- either and combination are possible at least)

(The fourth invention) W_{Ti}/W_{Zr} is set to 0.2-10, using TiO₂ equivalent-weight content of W_{Zr} and Ti as W_{Ti} for the ZrO₂ equivalent-weight content of Zr (the first - the third invention -- either and combination are possible at least)

[0024] An operation and effect of the composition of the second of the above-mentioned this invention are explained in detail below including an operation and effect of the above-mentioned first - the fourth invention. In the cover coat layer which makes the important section of the spark plug of the composition of the second of this invention, the feature is that it blended at 2 - 10% of the weight of a rate in total with the weight which carried out the oxide conversion of Ti and the Zr, respectively, stopping the sum total content range of an alkali-metal component in 12 or less (0 % of the weight being included) % of the weight of the range, and stopping the content range of B component to 20 - 35% of the weight by the weight which carried out oxide conversion at B₂O₃. By stopping the sum total content of an alkali-metal component, and the content of B component in the above-mentioned range, the effect which a cover coat layer with few defects of a foam etc. can be made easier for thickness to be uniform and to form is done so.

[0025] By cutting down the content of an alkali-metal component and B component, the reason the above effects are acquired is considered as follows. That is, in the manufacture method of this invention mentioned later, if there are many loadings of an alkali-metal component and B component in case cover coat powder is prepared as a cover coat slurry, these components are eluted in slurry solvents, such as water, and the viscosity of a slurry may be raised. If the viscosity of a slurry becomes extremely high, possibility that will be hard coming to obtain a uniform cover coat powder application layer, and a foam

etc. will be involved in will also become high (if it becomes high, for example exceeding 1000 mPa-s). However, viscosity becomes possible [preparing easily the cover coat slurry which is small rich in a fluidity] by choosing the content range of the above alkali-metal components and B component, and it is thought that thickness is uniform and it becomes easy to obtain a cover coat layer with few defects.

[0026] In addition, although it led to rising, the softening temperature, i.e., the glost firing temperature, of a cover coat, when the content of an alkali-metal component and B component decreased, in order to suppress elevation of this softening temperature, a lot of PbO(s) were conventionally blended into the cover coat, as already explained. However, with the second composition of the above, it has succeeded in cutting down the content of Pb component sharply, and specifically considering as 0.1 or less % of the weight by PbO conversion by replacing with PbO and blending the oxide component of Ti and Zr system, suppressing softening-temperature elevation of a cover coat. Therefore, the second technical problem of said this invention is solved. In addition, as for Pb component, it is still more desirable not to contain substantially except for what is mixed unescapable from a cover coat raw material etc.

[0027] Moreover, since the difference of coefficient of linear expansion with this is comparatively small when the insulator of a ground consists of for example, alumina system insulating materials, it is hard to produce a cracking crack etc. in the cover coat layer obtained. And rather than the cover coat of the conventional lead silicate glass system, a softening temperature is low and can carry out [low temperature]-izing of the glost firing temperature with 800-950 degrees C. Therefore, when performing glost firing simultaneously with the above-mentioned glass-seal process, it is hard to produce oxidization to a center electrode, the terminal metallic ornaments mentioned later. Furthermore, since the content of an alkali-metal component is cut down, the insulation (as a result, flashover-proof nature) of a cover coat layer is good. Moreover, even when the water resistance or chemical resistance of a cover coat layer obtained by blending the oxide component of Ti and Zr system is improved, for example, the alkali-metal component in a cover coat layer contains, the elution is suppressed and it contributes to the improvement in a withstand-voltage performance of a cover coat layer. About Zr component, the chemical-resistant improvement effect of a cover coat layer is much more remarkable as compared with Ti component. in addition, "water resistance is good here" -- for example, when a cover coat frit besides the ability of the component elution to the water from the formed cover coat layer not to take place easily is left in the form of an aqosity slurry for a long time, it also means that it is hard coming to generate the fault to which the viscosity of the slurry by component elution becomes high

[0028] When the sum total content of an alkali-metal component exceeds 12 % of the weight by oxide conversion, it becomes impossible for effects peculiar to this second composition, such as a fluid improvement effect of a cover coat slurry as a result equalization of the cover coat layer thickness obtained, or defective reduction, to attain notably in the second composition. Moreover, also in the point of insulating reservation of a cover coat, blending an alkali-metal component exceeding the above-mentioned range acts disadvantageously. It is also possible to cut down on the other hand, even on the level which is not substantially contained about the above-mentioned alkali-metal component except for what is mixed unescapable, for example from a cover coat raw material etc., since softening temperature elevation is suppressed by combination of the cover coat layer Ti and the oxide component of Zr system. For example, it is making the content into less than 5 % of the weight desirably less than 6% of the weight, and it can be said that the insulating disposition top effect by alkali-metal component curtailment can be attained much more notably. In addition, when a certain amount of alkali-metal component must be blended for glost firing temperature, a fluid improvement of a melting cover coat layer, etc., it is more effective like said first composition to ***** two or more sorts of alkali-metal components on on an insulating disposition.

[0029] Next, if the sum total content of Ti and Zr will be less than 2% of the weight by the weight which carried out oxide conversion, the softening temperature elevation depressor effect of a cover coat may be insufficient, and the glost firing in expected temperature may become impossible. On the other hand, if this sum total content exceeds 10 % of the weight, the fault the cover coat layer obtained by glost firing becomes easy to devitrify will be produced. Moreover, although the oxide of Ti and Zr is contributed to the softening-temperature fall of a cover coat by the eutectic reaction with other oxide components etc. when optimum dose combination is carried out for example, these oxides may cause the fault from which the softening temperature of a cover coat rises conversely, and becomes impossible [the glost firing in expected temperature], when it is essentially a high-melting point oxide and a sum total content exceeds 10 % of the weight, if independent. As for the sum total content by oxide conversion of Ti and Zr, it is good to consider as 3 - 8 % of the weight desirably.

[0030] In addition, since Zr component has the inclination a little larger than Ti component to which the

viscosity of a melting cover coat is made to increase, it raises the fluidity of a melting cover coat, and is more uniform, and it is good [component] like the second invention of the above to make the content of Zr component into 3.0 or less % of the weight desirably 3.4 or less % of the weight with ZrO₂ equivalent-weight content in the viewpoint which forms the cover coat layer excellent in appearance.

[0031] On the other hand, about Ti component, if it compares with Zr component, since there is little influence of a viscous increase of a melting cover coat, the cover coat layer which was excellent in making TiO₂ equivalent-weight content into 1.5 % of the weight or more like the third invention of the above water resistance or chemical-resistant can be formed good.

[0032] In addition, if Ti component becomes superfluous, when the coefficient of linear expansion of a cover coat layer becomes low too much and the insulator of a ground consists of for example, alumina system insulating materials, faults, such as intrusion (crazing), may occur in a cover coat layer according to the difference of the coefficient of linear expansion. Therefore, it excels water resistance or chemical-resistant, canceling such fault, and the fluidity of a melting cover coat is raised, it is uniform, and in order to obtain the good cover coat layer of appearance, it is desirable to ***** Ti component and Zr component. Specifically, it is good like said fourth invention to set W_{Ti}/W_{Zr} to 0.2-10, using TiO₂ equivalent-weight content of W_{Zr} and Ti as W_{Ti} for the ZrO₂ equivalent-weight content of Zr. When W_{Ti}/W_{Zr} became less than 0.2, and the contents of Ti component become easy to run short relatively and fully tend to acquire the waterproof or chemical-resistant improvement effect, it cannot but stop increasing the content of Zr component. Consequently, the viscosity of a melting cover coat increases and it becomes easy to produce the poor appearance of a cover coat layer. When W_{Ti}/W_{Zr} exceeded 10 and it is fully going to acquire the waterproof or chemical-resistant improvement effect, it cannot but stop on the other hand, increasing the content of Ti component. Consequently, the coefficient of linear expansion of a cover coat layer becomes low too much, and it becomes easy to generate a crazing etc. In addition, as for W_{Ti}/W_{Zr}, it is good to be desirably referred to as 0.5-7.

[0033] In the second composition of the above, Si component content in a cover coat is set as SiO₂ to 20 - 40% of the weight by the weight which carried out oxide conversion. If this Si component content becomes less than 20% of the weight when the insulator of a ground consists of alumina system insulating materials, the coefficient of linear expansion of a cover coat will become large too much, and it will become easy to produce defects, such as a cracking crack, in a cover coat layer. On the other hand, if this Si component content exceeds 40 % of the weight, the coefficient of linear expansion of a cover coat will become small too much conversely, and it will become easy to produce defects, such as intrusion (crazing), in a cover coat layer. In addition, defective generating of intrusion in a cover coat layer etc. can be made much more hard to produce because this Si component content carries out to below 38% weight like the first invention of the above. In addition, as for Si component content, it is good more desirably to set up in 25 - 35% of the weight of the range in SiO₂ oxide equivalent weight.

[0034] Moreover, in the second composition, B component content is set as B₂O₃ to 20 - 35% of the weight by the weight which carried out oxide conversion. If this B component content becomes less than 20% of the weight, the softening temperature of a cover coat will rise and the glost firing in expected temperature (the above-mentioned 800-950 degrees C) will become impossible. When B component content exceeds 35 % of the weight, it becomes impossible on the other hand, for effects peculiar to the second composition, such as a fluid improvement effect of a cover coat slurry as a result equalization of the cover coat layer thickness obtained, or defective reduction, to attain notably. moreover, phase splitting is produced in the cover coat layer obtained, and a cover coat layer devitrifies or it acts disadvantageously also in the point which becomes easy to produce problems, such as an insulating fall or coefficient-of-linear-expansion nonconformance with a ground In addition, as for this B component content, it is good to set up in 20 - 28% of the weight of the range desirably.

[0035] In addition, as for the sum total content (oxide conversion) of B component and an alkali-metal component, in the viewpoint which heightens the fluid improvement effect of a cover coat slurry, it is desirably good to consider as 35 or less % of the weight 42 or less % of the weight. Moreover, as for the sum total content (oxide conversion) with an alkali-metal component, Ti, and Zr component, in the viewpoint which suppresses too much rise of glost firing temperature, it is desirable to secure to 8% of the weight or more.

[0036] Next, in the second composition, Zn component content is set as ZnO in 15 - 25% of the weight of the range by the weight which carried out oxide conversion. If this Zn component content will be less than 15% of the weight, the softening temperature of a cover coat rises too much, and the glost firing in expected temperature may become impossible. On the other hand, if this Zn component content exceeds 25

% of the weight, the coefficient of linear expansion of a cover coat will become large too much, and it will become easy to produce defects, such as a cracking crack, in a cover coat layer. In addition, as for the content of this Zn component, it is desirably good to set up in 17 - 20% of the weight of the range still more desirably 15 to 20% of the weight.

[0037] Moreover, in the second composition, Ba component content is set as BaO in 10 - 23% of the weight of the range by the weight which carried out oxide conversion. If Ba component content will be less than 10% of the weight, the insulation of a cover coat falls and flashover-proof nature may be spoiled. On the other hand, if Ba component content exceeds 23 % of the weight, the softening temperature of a cover coat may rise and the glost firing in expected temperature may become impossible. In addition, as for the content of this Ba component, it is good to set up in 12 - 18% of the weight of the range desirably.

[0038] In addition, although it will set in the first composition of the spark plug of this invention, and the second composition and the above-mentioned cation component or auxiliary cation component in a cover coat will mainly be contained in the form of an oxide, the existence form by the oxide cannot be directly identified in many cases according to the factor of forming an amorphous glass phase. In this case, if the content of the element component in the value in a cover coat layer which carried out [aforementioned] oxide conversion is the thing of the above-mentioned range, it will be regarded as the thing belonging to the range of this invention.

[0039] Here, the content of each cation component of the cover coat layer formed on the insulator can be identified using the well-known microprobe-analysis methods, such as EPMA (electron-probe microprobe analysis) and XPS (X-ray photoelectron spectroscopy). For example, when using EPMA, you may use any of a wavelength-dispersion method and an energy-dispersion method for measurement of a characteristic X ray. Moreover, a cover coat layer is exfoliated from an insulator and there is also the method of carrying out composition identification of this a chemical analysis or by carrying out gas analysis.

[0040] moreover, the spark plug of this invention which has the above-mentioned cover coat layer -- the inside of the breakthrough of an insulator -- setting -- a center electrode and one -- or it can constitute as a thing equipped with the terminal metallic-ornaments section of the shape of a shaft established on both sides of the conductive binder course at the center electrode and another object in between In this case, this whole spark plug can be held at about 500 degrees C, and insulating resistance can be measured by energizing between the terminal metallic-ornaments section and subject metallic ornaments through an insulator. And in order to secure the insulating endurance in an elevated temperature, it is desirable [this insulating resistance] to secure 200 M omega or more, when preventing generating of a flashover etc.

[0041] Drawing 8 shows an example of the system of measurement. That is, while connecting a direct-current constant voltage power supply (for example, supply voltage 1000V) to the terminal metallic-ornaments 13 side of a spark plug 100, the subject metallic-ornaments 1 side is grounded, and it energizes in the state where have arranged the spark plug 100 in a heating furnace, and it heated at 500 degrees C. For example, considering the case where the energization current value I_m is measured using the resistance for amperometries (resistance R_m), the insulating resistance R_x which should be measured can be calculated in $(VS/I_m) \cdot R_m$ by setting energization voltage to VS (drawing, the energization current value I_m is measured by the output of the differential amplifier which amplifies the ends voltage difference of the resistance for amperometries).

[0042] Moreover, an insulator can constitute aluminum component from an alumina system insulating material contained 85 to 98% of the weight by the weight which carried out oxide conversion to aluminum $2O_3$. In this case, as for a cover coat, it is desirable for the coefficient of linear expansion of an average of the cover coat in a 20-350-degrec C temperature requirement to be the thing of the range of $50 \times 10^{-7}/\text{dcgrec-C} - 85 \times 10^{-7}/\text{degrec C}$. If coefficient of linear expansion is smaller than this lower limit, it will become easy to produce defects, such as intrusion (crazing), in a cover coat layer. On the other hand, if coefficient of linear expansion is larger than this upper limit, it will become easy to produce defects, such as a cracking crack, in a cover coat layer. In addition, as for the above-mentioned coefficient of linear expansion, it is good that it is the thing of the range of $60 \times 10^{-7}/\text{degrec-C} - 80 \times 10^{-7}/\text{degrec C}$ more desirably.

[0043] Here, the coefficient of linear expansion of a cover coat can start a sample from the glassy cover coat bulk object which blended and dissolved the raw material and obtained it so that it may become a cover coat layer and abbreviation same composition, and it can presume it with the value measured by the well-known dilatometer etc. using this. Moreover, the coefficient of linear expansion of the cover coat layer on an insulator can be measured using a laser interferometer, an atomic force microscope, etc.

[0044] Next, the first composition of the above-mentioned spark plug can be manufactured by the first of

the manufacture method of the following this inventions. This method Namely, Si, B, Zn, and Ba as a cation component, The source powder of a component used as two sorts (***** alkali-metal component) chosen from Na, K, and Li of each sources of a component B component to B-2 O3 18 to 35% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the Si component SiO2 25 - 40 % of the weight, While blending so that it may become 7 - 20 % of the weight ten to 25% of the weight by the weight which carried out the oxide conversion of the Ba at BaO with the weight which carried out the oxide conversion of the Zn component at ZnO About a ***** alkali-metal component, Na2O and K Na K2O, By the weight which carried out oxide conversion, Li is blended with Li2O three to 9% of the weight, respectively. After mixture, The cover coat powder manufacture process of preparing cover coat powder using the frit which was made heated and carrying out melting of the mixture to 1000-1500 degrees C, quenched and vitrified the melt, and was ground, A cover coat layer and the glost firing process to make are included by printing a cover coat powder deposit on an insulating body surface the cover coat powder deposition process which is made to deposit the cover coat powder on the surface of an insulator, and forms a cover coat powder deposit, and by calcinating the insulator in a 800-950-degree C temperature requirement.

[0045] Moreover, the second composition of the above-mentioned spark plug can be manufactured by the second of the manufacture method of the following this inventions. This method Namely, Si, B, Zn, and Ba as a main cation component, The source powder of a component used as at least one sort of each sources of a component chosen from Ti and Zr B component to B-2 O3 20 to 40% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the Si component SiO2 20 - 35 % of the weight, While containing Ba component ten to 23% of the weight in BaO 15 to 25% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the Zn component at ZnO, Ti and Zr It blends so that it may become what is contained two to 10% of the weight in total by the weight in which carried out Ti TiO2 and Zr carried out oxide conversion ZrO2, respectively. After mixture, The cover coat powder manufacture process of preparing cover coat powder using the frit which was made heated and carrying out melting of the mixture to 1000-1500 degrees C, quenched and vitrified the melt, and was ground, It is characterized by including a cover coat layer and the glost firing process to make by printing a cover coat powder deposit on an insulating body surface the cover coat powder deposition process which is made to deposit the cover coat powder on the surface of an insulator, and forms a cover coat powder deposit, and by calcinating the insulator in a 800-950-degree C temperature requirement.

[0046] In addition, as source powder of a component of each component (in making an auxiliary cation component besides the source powder of a component of a cation component contain, it also contains the source powder of a component), various inorganic system material powder, such as a hydroxide besides the oxide (a multiple oxide is sufficient) of these components, a carbonate, a chloride, a sulfate, a nitrate, and phosphate, can be used. What can be converted into an oxide by heating and melting needs to be used for each these inorganic system material powder. Moreover, the method of injecting a melt besides the method of investing a melt underwater on a cooling roller front face, and obtaining a flakes-like rapid solidification object can also be used for quenching.

[0047] Cover coat powder can be prepared as a cover coat slurry which distributed the above-mentioned frit in water or the solvent. In this case, a cover coat powder deposit can be formed as an application layer of this cover coat slurry by applying a cover coat slurry to an insulating body surface, and drying. In addition, if the method of spraying a cover coat slurry on an insulating body surface from a spraying nozzle is used as a method of applying a cover coat slurry to an insulating body surface, the cover coat powder deposit of uniform thickness can be formed easily, and adjustment of the application thickness is also easy.

[0048] The clay mineral and the organic binder of a proper quantity can be blended with a cover coat slurry in order to heighten the configuration holding power of the formed cover coat powder deposit. What can use what is constituted by the subject in a water aluminosilicate, for example, makes a subject one sort (or those composites), such as an allophane, an imogolite, a HISHINGE light, a smectite, a kaolinite, a halloysite, a montmorillonite, an illite, a vermiculite, and a dolomite, or two sorts or more can be used for a clay mineral. Moreover, in addition to SiO2 and aluminum 2O3, in the viewpoint of the oxide system component to contain, what mainly contains one sort, such as Fe 2O3, TiO2, CaO and MgO, Na2O, and K2O, or two sorts or more can be used.

[0049] While terminal metallic ornaments are fixed to the edge side of one of these and a center electrode is similarly fixed to an other-end section side to the breakthrough formed in the shaft orientations of an insulator, the spark plug of this invention It can constitute as that in which the sintering electrical-

conducting-material section (for example, a conductive glass-seal layer and a resistor) which mainly consists of mixture of glass and a conductive material in order to join them electrically between terminal metallic ornaments and a center electrode into this breakthrough was formed. When manufacturing this, a method including the following processes can be adopted. - Assembly manufacturing process : while terminal metallic ornaments are arranged at the edge side of one of these and a center electrode is similarly arranged to the breakthrough of an insulator at an other-end section side, manufacture the assembly in which the packed bed of the sintering electrical-conducting-material raw material powder which makes a subject the end of a glass powder and conductive material powder between terminal metallic ornaments and a center electrode was formed in this breakthrough. - Glost firing process : heat the assembly in the state where the cover coat powder deposit was formed on the surface of the insulator, to a 800-950-degree C temperature requirement, print a cover coat powder deposit on an insulating body surface, and perform simultaneously a cover coat layer, the process to make, and the process which softens the glass-powder end in a packed bed. - Press process : in the heated assembly, by making a center electrode and terminal metallic ornaments approach relatively within a breakthrough, press a packed bed between these center electrodes and terminal metallic ornaments, and make with the sintering electrical-conducting-material section.

[0050] In this case, while terminal metallic ornaments and a center electrode are electrically joined by the sintering electrical-conducting-material section, between the inside of an insulator breakthrough, these terminal metallic ornaments, and center electrodes seals (seal). Therefore, the above-mentioned glost firing process and a press process will form a glass-seal process. Since a glass-seal process and a glost firing process are simultaneously made by this method, it is efficient. Moreover, since the above-mentioned cover coat is used and glost firing temperature can be made low with 800-950 degrees C, it is hard to generate the poor manufacture by oxidization of a center electrode or terminal metallic ornaments, and the product yield of a spark plug improves.

[0051] In this case, as for the softening temperature of a cover coat, it is good to adjust in 600-700 degrees C. If a softening temperature exceeds 700 degrees C, the glost firing temperature of 950 degrees C or more will be needed, and oxidization of a center electrode or terminal metallic ornaments will become easy to progress. On the other hand, if a softening temperature becomes less than 600 degrees C, the need of also setting glost firing temperature as less than 800-degree C low temperature will arise. The glass used for the sintering electrical-conducting-material section must also stop in this case, also having to use the low thing of a softening temperature so that a good glass-seal state may be acquired. Consequently, when the glass in the sintering electrical-conducting-material section becomes easy to deteriorate when the completed spark plug is used under comparatively hot environment for a long time, for example, the sintering electrical-conducting-material section contains a resistor, it may lead to degradation of performances, such as the load life property.

[0052] In addition, the softening temperature of a cover coat says what was measured as follows. That is, the glassy cover coat bulk object which blended and dissolved the raw material and obtained it is pulverized, and it considers as the particle size of 10 micrometers - about 100 micrometers. Differential thermal analysis is performed reheating this and it considers as this softening temperature with the temperature of the peak (namely, endothermic peak generated in the 2nd) which appears in the degree of the first endothermic peak showing ***** moreover, about the softening temperature of the cover coat layer formed in the insulating body surface So that the composition which analyzed the content of the aforementioned cation component in a cover coat layer and the aforementioned auxiliary cation component, respectively, and carried out oxide conversion may be computed and it may become almost equal to this composition The oxide raw material of each ***** element component shall be quenched after combination / dissolution, a glass sample shall be obtained, and the softening temperature of the formed cover coat layer concerned shall be presumed with the softening temperature of the glass sample.

[0053] Next, the insulator which should form the above-mentioned cover coat layer is an insulating material which makes an alumina a principal component, and can consist of insulating materials which contain Na component in 0.07 - 0.5% of the weight of the range by Na₂O conversion. In addition, especially when Na component content is called below, unless it refuses, the content made all Na₂O conversion shall be meant.

[0054] In recent years, in the spark plug used for internal combustion engines, such as an automobile engine, the material of the alumina (aluminum 2O₃) system which was excellent in thermal resistance as a material of the insulator is used for many years. That (henceforth a buyer alumina) by which the above raw material aluminas of an insulating material were generally manufactured by the buyer (Bayer) method is

used.

[0055] Although a Bayer process is law which carries out wet extraction of the alumina from the bauxite which is an aluminum raw-ore stone, caustic-alkali-of-sodium (NaOH) solution with comparatively high concentration is used as extraction intermediation. Therefore, since the buyer alumina obtained becomes a thing containing Na component (a part for soda) of a considerable amount, it is used in the form where ** soda treatment was given if needed. and the grade of the ** soda -- responding -- for example, the content of Na component -- 0.05 or less % of the weight of a thing -- a low soda alumina -- similarly the common name of the thing beyond an inside soda alumina and what [about] has more Na components than it, for example, 0.2 % of the weight, and it is usually carried out for about 0.1 - 0.2% of the weight of the thing to the soda alumina etc.

[0056] By the way, Na component contained in an alumina will produce insulating resistance and the fault of reducing the insulating resistance in an elevated temperature of 500 degrees C or more especially, or spoiling the mechanical strength in an elevated temperature, if the content becomes superfluous in order to show high ion conductivity. Therefore, conventionally the alumina system insulating material currently used for the spark plug is made good [what has the content of Na component few if possible], and it has been common sense to set the Na component content as 0.05 or less % of the weight of a low value.

[0057] Here, in order to manufacture the low alumina system insulator of Na component content as mentioned above, it is indispensable that the raw material alumina to be used also uses the thing of a low soda system. The above-mentioned passes along the alumina of a low soda system, only its part which needs a ** soda process is expensive, and it has the side it cannot necessarily be said that is desirable from a viewpoint of raw material cost. However, in connection with high increase in power, such as an automobile engine, still higher withstand-voltage property and thermal resistance have been required also from the insulator of a spark plug in recent years. Consequently, the present condition is the above-mentioned common sense about Na component content in an insulating material being still firmer, and also admitting some cost quantities depended on low-soda-alumina use.

[0058] However, when this invention person examined wholeheartedly Na component content of the alumina system insulating material for spark plugs, he found out that the insulating material of the performance in which insulation resistance, a mechanical strength, etc. in an elevated temperature do not fall unexpectedly, but rival the conventional insulating material with Na component content lower than this was obtained in the high composition range of the above-mentioned Na component content it was considered until now that was the outside of common sense. Furthermore, in this invention, it can be said that it is advantageous when an insulator is constituted from a high alumina system ceramic of the above Na component contents, since good insulation is secured by two kinds chosen as a cover coat layer from Na, K, and Li being ***** (ed).

[0059] And the alumina powder used as a raw material can also use what has as high at Na₂O conversion Na component content as 0.07 - 0.65 % of the weight by Na component content being set as the above ranges (when it exceeds 0.65 % of the weight, it becomes impossible to maintain Na component content in the insulating material obtained to 0.5 or less % of the weight). Consequently, it replaces with the conventional low soda alumina, and a far cheap inside soda alumina and dramatic manufacturing-cost curtailment in the spark plug for which a soda alumina etc. can usually be used now and insulator ***** for spark plugs used it are realized.

[0060] In order to make Na component content in an insulating material into less than 0.07 % of the weight, it becomes impossible in addition, to have to use the low alumina powder of Na component contents, such as a low soda alumina, and to secure a predominance on the raw material cost to the conventional insulating material. When Na component content exceeds 0.5 % of the weight, the value of the insulation resistance of material becomes inadequate and it becomes impossible on the other hand, to satisfy the withstand-voltage performance required of the insulator for spark plugs. As for Na component content in an insulating material, it is good to consider as 0.07 - 0.25 % of the weight more desirably. Moreover, as for the alumina powder used as a raw material, it is good that Na component content uses 0.07 - 0.3% of the weight of a thing by Na₂O conversion desirably.

[0061] What was manufactured by the Bayer process can be used as alumina powder used for manufacture of the above-mentioned insulating material. In addition, the usual buyer alumina powder hardly contains alkali-metal components other than Na component (henceforth non-Na alkali-metal component), if what is contained as an unescapable impurity is removed. Therefore, when such buyer alumina powder is used, the sum total content of non-Na alkali-metal component in the insulating material obtained becomes 0.05 or less % of the weight of a thing by oxide conversion, unless those positive addition is performed.

[0062] Moreover, when this invention person inquired further wholeheartedly, although Na component was contained also inside the powder particle at the alumina powder obtained by the Bayer process, it turns out that Na component has condensed in the surface section of a powder particle on the relation processed by the solution of caustic alkali of sodium. And at the time of baking, such a Na component of the surface section of a powder particle is fused with a sintering-acid component (the below-mentioned alloying-element component), and makes a glass phase. This glass phase has the problem which leads to the fall of the insulating resistance of material, or an insulating withstand voltage, as a result of electric specific resistance's falling because Na component dissolves, and this acting as a track.

[0063] And as a result of this invention person's inquiring further in view of this, the alumina powder to be used was understood that it is good that the content of Na component which exists in the surface section of particle powder uses what is 0.01 - 0.2 % of the weight by Na₂O conversion. If the content of Na component of the powder surface section uses the alumina powder exceeding 0.2 % of the weight, the insulating resistance and insulating withstand voltage of an insulating material which are obtained may be insufficient. In order to carry out the content of Na component which exists in the surface section of a powder particle to less than 0.01% of the weight, even when the low alumina powder of Na component contents, such as a low soda alumina, must be used after all or it uses the high alumina powder of Na component content, the process which removes Na component of the powder particle surface section by washing etc. is needed, and it becomes impossible moreover, to secure a predominance on the raw material cost to the conventional insulating material. In addition, as for the content of Na component which exists in the surface section of particle powder, it is good that it is 0.01 - 0.1 % of the weight more desirably.

[0064] Here, "the content of Na component which exists in the surface section of a powder particle" means the value measured as follows. First, the total content (unit : % of the weight) of Na component in the alumina powder used as the measuring object is measured by ICP analysis, the chemical analysis, etc., the Na₂O conversion of the value are done, and it is referred to as WNa1. Subsequently, it carries out being 1hr immersed in the state where stirring is not added into 1l. of distilled water which held 100g of alumina powder in temperature of 90 degrees C. Then, separation recovery of the alumina powder is carried out, Na component content (unit : % of the weight) is measured again, the Na₂O conversion of the value are done, and it is referred to as WNa2. And let value WNa1-WNa2 (unit : % of the weight) which reduced WNa1 to WNa2 measured previously be the content of Na component which exists in the surface section of a powder particle.

[0065] In this case, the organization of the insulating material obtained is mainly constituted by alumina system matrix **** whose alumina content is 99 % of the weight, and the glass phase formed in the grain-boundary section of the alumina system matrix ****. Here, although it exists in a glass phase among Na components in an insulating material, as for Content WGN_a, it is good that it is 0.4 - 2 % of the weight by Na₂O conversion. If this WGN_a exceeds 2 % of the weight, the insulating resistance and insulating withstand voltage of an insulating material may be insufficient. In order to consider as less than 0.4 % of the weight, it becomes impossible moreover, to have to use the low alumina powder of Na component content, and to secure a predominance on the raw material cost to the conventional insulating material.

[0066] In addition, Above WGN_a shall adopt the value computed as follows in approximation in this specification. First, a material-list side is ground, organization observation of this is carried out with a scanning electron microscope (SEM) etc., the rate of area of an alumina system matrix phase (equivalent to the rate of volume in material) is measured in the analysis of the organization picture, and the value is set to gammaA. Subsequently, the weight concentration of average Na component in a glass phase is identified by well-known minute component-analysis methods (for example, EPMA (electron-probe microprobe analysis), EDS (energy-dispersion type X a segment light) or WDS (wavelength-dispersion type X a segment light), etc.), the Na₂O conversion of it are done, and it asks for it as NGN_a. And material is constituted by only the alumina system matrix phase and the glass phase. and the apparent density gravity of the material measured by the Archimedes method etc. while assuming that it had turned precisely nearly completely by sintering -- the density of rho 0 (unit : g/cm³) and alumina system crystal grain -- rho 1 (=3.97 g/cm³) -- then The weight MG of the glass phase which exists in per material unit volume is $MG = \rho_0 - \rho_1$ and gammaA..... Since it asks as (1), it is WGN_a. $WGN_a = MG \cdot NGN_a \cdot 100 = (\rho_0 - \rho_1) \cdot \gamma A$ and gammaA) and NGN_a x 100 (% of the weight) It is calculable (2).

[0067] In addition, it is good that the weight concentration NGN_a of average Na component in a glass phase is 0.4 - 2 % of the weight by Na₂O conversion for the same reason as the above.

[0068] Next, in the insulating material of this invention, it is good to adjust aluminum component content (for it to be hereafter described as WA1) in the weight converted into aluminum 2O₃ in 85 - 98% of the

weight of the range. If WAl will be less than 85% of the weight, the high temperature strength and withstand-voltage property of material may become inadequate. In addition, as for Above WAl, it is good to consider as 90 % of the weight or more desirably. However, if WAl exceeds 98 % of the weight, it becomes difficult for the amount of a sintering-acid component to decrease too much relatively, and to make a sintered compact turn precisely, if you are going to make it sinter precisely, sintering temperature rises, as a result, alumina grain growth is promoted, and the fault of intensity deteriorating on the contrary may be produced. So, as for this WAl, it is good to adjust in 98 or less % of the weight of the range.

[0069] moreover, one sort or two sorts or more of alloying-element components chosen from Si, calcium, Mg, Ba, Zn, B, and Na in the insulating material of this invention -- Si -- SiO₂ -- calcium -- CaO -- Ba can make ZnO contain Mg 0.1 to 15% of the weight in total in MgO at BaO by the weight to which carried out B at B-2 O₃, and Zn carried out the oxide conversion of Na at Na₂O, respectively As raw material powder for manufacturing such an insulating material The alloying-element system raw material which contains Si, calcium, Mg, Ba, Zn, and B to the alumina powder 85 - 98 weight sections, As for calcium, what was blended with MgO so that Ba might serve as 0.1 - 15 weight section in total at BaO by the weight when B is carried out at B-2 O₃ and Zn carries out the oxide conversion of Na at Na₂O, respectively is used for ZnO for Si by SiO₂ at CaO, as for Mg.

[0070] In addition, about each component of Si, calcium, Mg, Ba, and Zn, various inorganic system raw material powder, such as a hydroxide besides the oxide (a multiple oxide is sufficient) of these components, a carbonate, a chloride, a sulfate, a nitrate, and phosphate, can be used for an alloying-element system raw material. What can be converted into an oxide by baking needs to be used for each these inorganic system raw material powder. moreover -- B component -- various boric acids including an ortho boric acid (H₃BO₃) besides 3 oxidization 2 boron (B-2 O₃) -- further -- an insulator -- a major element -- aluminum, a borate with calcium, Mg, Ba, Zn, etc., etc. can be used

[0071] The above-mentioned alloying-element component is fused at the time of baking, produces the liquid phase, and functions as a sintering acid which promotes precise-ization. If the sum total content (it is hereafter described as W1) in the weight in which the alloying-element component in an insulating material carried out [above-mentioned] oxide conversion becomes less than 0.1% of the weight, it becomes difficult to make a sintered compact turn precisely, and the high temperature strengths of material and the withstand-voltage properties in an elevated temperature run short on the contrary. On the other hand, if W1 exceeds 15.0 % of the weight, it will lead to the high temperature strength of material being spoiled. So, as for the sum total content W1 of an alloying-element component, it is good that considering as 0.1 - 15.0 % of the weight considers as 3.0 - 10.0 % of the weight often and more desirably.

[0072] Among these, Ba component and B component also have the effect which raises the high temperature strength of an insulating material notably. And as for Ba component, it is good to make it contain 0.02 to 0.80% of the weight by the weight (for it to be hereafter described as WBaO) converted into BaO. When WBaO becomes less than 0.02% of the weight, the effect of the improvement in a high temperature strength by BaO combination becomes less remarkable. Moreover, if WBaO exceeds 0.80 % of the weight, it will lead to the high temperature strength of material being spoiled. As for WBaO, it is good to adjust in 0.15 - 0.50% of the weight of the range desirably. On the other hand, as for B component, it is good to make it contain 0.01 to 0.75% of the weight by the weight (for it to be hereafter described as WB 2O₃) converted B-2O₃. When WB 2O₃ becomes less than 0.01% of the weight, the effect of the improvement in a high temperature strength by 2OWB3 combination becomes less remarkable. Moreover, if WB 2O₃ exceeds 0.75 % of the weight, it will lead to the high temperature strength of material being spoiled. As for WB 2O₃, it is good to adjust in 0.15 - 0.50% of the weight of the range desirably.

[0073] In addition, in order to operate an alloying-element component more effectively as a sintering acid, it is important to generate the fluid good liquid phase the neither more nor less at the predetermined sintering temperature set as low temperature rather than aluminum 2O₃. For that, it is more effective to mix two or more kinds together and to blend in many cases rather than blending each component independently. For example, when blending all of the five above-mentioned kinds of first addition components in the form of an oxide The material finally obtained contains Si component 1.50 to 5.00% of the weight by the weight converted into SiO₂. calcium component is contained 1.20 to 4.00% of the weight by the weight converted into CaO. It is desirable that it is what contains 0.05 to 0.17% of the weight by the weight which converted Mg component into MgO, contains 0.15 to 0.50% of the weight by the weight which converted Ba component into BaO, and is contained 0.15 to 0.50% of the weight by the weight which converted B component into B-2 O₃.

[0074]

[Embodiments of the Invention] Hereafter, it explains with reference to some examples which show the form of operation of this invention to a drawing.

(Example 1) Drawing 1 and drawing 2 show one example of the spark plug concerning the first composition of this invention. This spark plug 100 While an end is combined with the insulator 2 which it *****cd inside the subject metallic ornaments 1, the center electrode 3 prepared inside the insulator 2 in the state where the ignition section 31 formed at the nose of cam was made to project, and the subject metallic ornaments 1 by welding etc. so that the tubed subject metallic ornaments 1 and a point 21 may project It has the grounding-electrode 4 grade arranged so that an other end side may be bent again in the side and the side may counter with the point of a center electrode 3. Moreover, the ignition section 32 which counters the above-mentioned ignition section 31 is formed in the grounding electrode 4, and let the crevice between these ignition section 31 and the ignition section 32 which counters be the spark discharge gap g.

[0075] While the subject metallic ornaments 1 are formed in the shape of a cylinder with metals, such as low-carbon steel, and constituting housing of a spark plug 100, the thread part 7 for attaching in the cylinder crank case which does not illustrate a plug 100 is formed in the peripheral face. In addition, in case 1e attaches the subject metallic ornaments 1, it is the tool engagement section with which tools, such as a spanner and a wrench, are made to engage, and has the axial hexagon-head-like cross-section configuration.

[0076] Next, the breakthrough 6 is formed in the shaft orientations of an insulator 2, the terminal metallic ornaments 13 are inserted and fixed from the edge side of one of these, and, similarly the center electrode 3 is being inserted and fixed from the other-end section side. Moreover, the resistor 15 is arranged between the terminal metallic ornaments 13 and the center electrode 3 in this breakthrough 6. The both ends of this resistor 15 are electrically connected to a center electrode 3 and the terminal metallic ornaments 13 through the conductive glass-seal layers 16 and 17, respectively. These resistors 15 and the conductive glass-seal layers 16 and 17 constitute the sintering electrical-conducting-material section. In addition, a resistor 15 consists of resistor constituents obtained by using the mixed-powder end of the end of a glass powder, and electrical-conducting-material powder (and accepting the need ceramic powder other than glass) as a raw material, and carrying out hot press of this in the below-mentioned glass-seal process. In addition, it is good also as composition which omitted the resistor 15 and unified the terminal metallic ornaments 13 and the center electrode 3 by much more conductive glass-seal layer.

[0077] An insulator 2 has the breakthrough 6 for inserting a center electrode 3 in the interior in accordance with own shaft orientations, and the whole is constituted by the following insulating materials. That is, this insulating material is constituted by the subject in an alumina, and consists of weights which converted aluminum component into aluminum $2O_3$ as an alumina system ceramic sintered compact which carries out content 85 to 98% of the weight (desirably 90 - 98 % of the weight).

[0078] The following can be illustrated as concrete composition of components other than aluminum.

Si component: It is SiO_2 equivalent weight and is 1.50 - 5.00 % of the weight.;

calcium component: It is CaO equivalent weight and is 1.20 - 4.00 % of the weight.;

Mg component: It is equivalent weight at MgO and is 0.05 - 0.17 % of the weight.;

Ba component: It is equivalent weight at BaO and is 0.15 - 0.50 % of the weight.;

B component: It is B_2O_3 equivalent weight and is 0.15 - 0.50 % of the weight.

[0079] As shown in drawing 1, lobe 2e which projects outward [hoop-direction] is formed in the shaft-orientations middle of an insulator 2 for example, in the shape of a flange. And the back side is set to this soma 2b formed in the narrow diameter by this rather than this lobe 2e at the insulator 2 by making into a front side the side which goes at the nose of cam of a center electrode 3 (drawing 1). On the other hand, second shank 2i of further a narrow diameter is formed in the front side of lobe 2e in this sequence from the 2g of the first shank and the 2g of the first shank of a narrow diameter [this]. In addition, corrugation section 2c is formed in the peripheral face back end section of this soma 2b. Moreover, the peripheral face of the 2g of the first shank is made approximate circle tubed, and the peripheral face of second shank 2i is made into the shape of the approximate circle conical surface whose diameter is reduced, so that it goes at a nose of cam.

[0080] On the other hand, the diameter of an axial cross section of a center electrode 3 is set up smaller than the diameter of an axial cross section of a resistor 15. And the breakthrough 6 of an insulator 2 has approximate circle tubed part I part 6a in which a center electrode 3 is made to insert, and approximate circle tubed part II part 6b by which it is formed by the twist at a major diameter in the back side (drawing upper part side) of the part I part 6a. As shown in drawing 1, the terminal metallic ornaments 13 and a resistor 15 are held in part II part 6b, and a center electrode 3 is inserted in in part I part 6a. It projects

outward from the peripheral face, and heights 3c for electrode fixation is formed in the back end section of a center electrode 3. And part I part 6a of the above-mentioned breakthrough 6 and part II part 6b are mutually connected into the 2g of the first shank of drawing 4 (a), and heights receptacle side 6c for receiving heights 3c for electrode fixation of a center electrode 3 in the connecting location is formed a taper side or in the shape of an R side.

[0081] Moreover, the peripheral face of 2h of connections with the 2g of the first shank and second shank 2i is used as a joggled aspect, and ***** of shaft orientations is made by being engaged through the board packing 63 of the shape of protruding line section 1c as the subject metallic-ornaments side engagement section by which this was formed in the inside of the subject metallic ornaments 1, and a ring. On the other hand, between the back side opening inside of the subject metallic ornaments 1, and the external surface of an insulator 2, the line packing 62 of the shape of a ring which engages with the back side periphery of flange-like lobe 2e is arranged, and the ring-like line packing 60 is arranged through the packed beds 61, such as talc, at the back side at the pan. And an insulator 2 is turned to the subject metallic ornaments 1, it pushes into a front side, the opening edge of the subject metallic ornaments 1 is turned to packing 60 in the state, 1d of caulking sections is formed inside of caulking ***** , and the subject metallic ornaments 1 are being fixed to the insulator 2.

[0082] Drawing 4 (a) and drawing 4 (b) show some examples of an insulator 2. The size of each part is illustrated below.

- Overall-length L1:30-75mm.
- Length L2:0-30mm of the 2g of the first shank (however, 2h of connections with second shank 2i is included excluding 2f of connections with lobe 2c).
- Length L3:2-27mm of second shank 2i.
- Outer-diameter D1:9-13mm of this soma 2b.
- Outer-diameter D2:11-16mm of lobe 2c.
- Outer-diameter D3:5-11mm of the 2g of the first shank.
- Diameter Dof end face outside4:3-8mm of second shank 2i.
- Point outer-diameter D5(however, when R or beveling is performed to apical surface periphery edge, in cross section containing medial-axis line O, outer diameter in end face position of this R section or the chamfering-of-the-edge section is pointed out):2.5-7mm of second shank 2i.
- Bore D6:2-5mm of part II part 6b of a breakthrough 6.
- Bore D7:1-3.5mm of part I part 6a of a breakthrough 6.
- Thickness t1:0.5-4.5mm of the 2g of the first shank.
- End face section thickness t2(value in sense which intersects perpendicularly with medial-axis line O):0.3-3.5mm of second shank 2i.
- Point thickness t3(when R or beveling is performed to value; however apical surface periphery edge in sense which intersects perpendicularly with medial-axis line O, in cross section containing medial-axis line O, thickness in end face position of this R section or the chamfering-of-the-edge section is pointed out):0.2-3mm of second shank 2i.
- Average-wall-thickness $tA(t2+t3) (/2)$:0.25-3.25mm of second shank 2i.

[0083] Moreover, in drawing 1, the length LQ of partial 2k projected to the back side of the subject metallic ornaments 1 of an insulator 2 is 23-27mm (for example, about 25mm). Furthermore, when the longitudinal section containing the medial-axis line O of an insulator 2 is taken, in the peripheral face of lobe part 2k of an insulator 2, length LP measured along with the cross-section visible outline until it reaches [from the position corresponding to the back end edge of the subject metallic ornaments 1] the back end edge of an insulator 2 through corrugation 2c is 26-32mm (for example, about 29mm).

[0084] In addition, the above-mentioned each part size in the insulator 2 shown in drawing 4 (a) for example, : which is as follows -- L -- 1 = about 60mm and L -- 2 = about 10mm and L3= -- about 14mm D -- 1 = about 11mm and D -- 2 = about 13mm and D -- 3 = about 7.3mm D 4= 5.3mm D 5= 4.3mm D 6= 3.9mm D 7= 2.6mm t 1= 3.3mm t 2= 1.4mm t 3= 0.9mm and tA=1.15mm

[0085] Moreover, the insulator 2 shown in drawing 4 (b) reaches the 2g of the first shank, and second shank 2i has a little large outer diameter as compared with what is shown in drawing 4 (a), respectively. :L whose size of each part is as follows -- L -- 1 = about 60mm and L2= -- about 10mm L -- 3 = about 14mm and D -- 1 = about 11mm and D -- 2 = about 13mm and D -- 3 = about 9.2mm D 4= 6.9mm D 5= 5.1mm D 6= 3.9mm D 7= 2.7mm t 1= 3.3mm t 2= 2.1mm t 3= 1.2mm and tA=1.65mm

[0086] Next, as shown in drawing 3, 2d of cover coat layers is formed in the front face of an insulator 2, the peripheral face of this soma 2b which specifically contains corrugation section 2c, and the peripheral

face of the 2g of the first shank. 10-150 micrometers of formation thickness of 2d of cover coat layers are desirably set to 20-50 micrometers. In addition, as shown in drawing 1, while 2d of cover coat layers formed in this soma 2b is formed in the form where the shaft-orientations front side enters predetermined length inside the subject metallic ornaments 1, the back side is prolonged to the back end marginal position of this soma 2b. On the other hand, 2d of cover coat layers formed in the 2g of the first shank is formed in the field from the shaft-orientations mid-position to 2h of connections which the board packing 63 contacts so that a surface of action with the inner skin of the subject metallic ornaments 1 may be included.

[0087] The main cation component 2d of cover coat layers Next, Si, B, Zn, and Ba. It consists of two sorts (***** alkali-metal component) chosen from Na, K, and Li. B component to B-2 O3 18 to 35% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the Si component SiO2 25 - 40 % of the weight, While containing Ba component seven to 20% of the weight in BaO ten to 25% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the Zn component at ZnO a ***** alkali-metal component -- Na -- Na2O and K2 -- O and Li are constituted from a weight which carried out oxide conversion by Li2O with the cover coat contained three to 9% of the weight, respectively

[0088] This cover coat Si component to SiO2 specifically by the weight which carried out oxide conversion 18 - 35 % of the weight, To ZnO Zn component 25 to 40% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the B component at B-2 O3 10 - 25 % of the weight, Na component to Na2O seven to 20% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the Ba component at BaO 3 - 9 % of the weight, K component is contained three to 9% of the weight in K2O by the weight which carried out oxide conversion, respectively, and the sum total content in the value in which Si component, B component, Zn component, Ba component, and the ***** alkali-metal component carried out each oxide conversion is made into 95 % of the weight or more. Even if this cover coat does not contain Pb component substantially or contains it, the content is 1.0 or less % of the weight of a thing by PbO conversion. To this cover coat, as an auxiliary cation component, moreover, aluminum, calcium, Fe, Zr, One sort of Ti, Sr, Mg, Bi, nickel, Sn, P, and Mn, or two sorts or more aluminum -- aluminum 2O3 -- calcium to CaO Zr for Fe ZrO2 at Fe 2O3 Ti -- TiO2 -- Sr -- SrO -- Mg -- MgO -- Bi may contain nickel in 5 or less % of the weight of the range in total in NiO at Bi 2O3 by the weight in which Sn carried out PP2O5 SnO2, and Mn carried out oxide conversion at MnO, respectively

[0089] Next, each of these somata 3a and 4a of a center electrode 3 and a grounding electrode 4 consist of nickel alloys etc. Moreover, core material 3b which consisted of Cu or a Cu alloy for heat dissipation promotion is laid under the interior of this soma 3a of a center electrode 3. On the other hand, the above-mentioned ignition section 31 and the ignition section 32 which counters are constituted by the subject in the precious alloy which makes a principal component one sort of Ir, Pt, and Rh, or two sorts or more. As shown in drawing 2 (b), this soma 3a of a center electrode 3 piles up the disc-like chip which consists of alloy composition which the apical surface is constituted evenly and constitutes the above-mentioned ignition section here while the diameter of a nose-of-cam side is reduced, and the ignition section 31 is formed by forming a weld zone W by laser welding, electron beam welding, resistance welding, etc. along with the plane-of-composition rim section further, and fixing this. Moreover, the ignition section 32 which counters carries out alignment of the chip to a grounding electrode 4 in the position corresponding to the ignition section 31, and is formed by forming a weld zone W similarly along with the plane-of-composition rim section, and fixing this. In addition, the sintering material obtained by fabricating and sintering the metal simple substance component powder blended by the dissolution material [which is obtained by blending and dissolving each alloy content so that it may become for example, notation composition], and of alloy powder, or predetermined ratio can constitute these chips. In addition, the ignition section 31 and the ignition section 32 which counters are good also as composition which omits at least one side.

[0090] The above-mentioned spark plug 100 is manufactured, for example by the following methods. First, although it is an insulator 2, this blends alumina powder and each source powder of a component of Si component, calcium component, Mg component, Ba component, and B component after baking as raw material powder by the predetermined ratio which serves as the above-mentioned composition by oxide conversion, adds and mixes the binder (for example, PVA) and water of the specified quantity, and makes the base slurry for fabrication. in addition, each source powder of a component -- for example, as for SiO2 powder and calcium component, in Si component, BaCO3 powder and B component can blend [MgO powder and Ba component] CaCO3 powder and Mg component in the form of H3BO3 powder In addition, you may blend H3BO3 in the form of a solution.

[0091] Spray drying of the base slurry for fabrication is carried out by the spray-drying method etc., and let it be a base granulation object for fabrication. And the press-forming object used as the original form of an insulator is made by carrying out rubber-press fabrication of the base granulation object for fabrication.

Drawing 9 shows the process of rubber-press fabrication typically. Here, the rubber die 300 which has the cavity 301 penetrated to shaft orientations is used for the interior, and lower punch 302 is inserted in bottom opening of the cavity 301. Moreover, in the punch side of lower punch 302, while being prolonged in the shaft orientations in a cavity 301, the press pin 303 which specifies the configuration of the breakthrough 6 (drawing 1) of an insulator 2 protrudes in one.
 [0092] In this state, it is filled up with the base granulation object PG for fabrication of the specified quantity in a cavity 301, and upper punch 304 closes top opening of a cavity 301, and it is sealed. A fluid pressure is impressed to the peripheral face of a rubber die 300 in this state, and the press-forming object 305 as shown in drawing 10 is acquired by compressing the granulation object PG of a cavity 301 through this rubber die 300. In addition, after the moisture of the 0.7 - 1.3 weight section is added by making the weight of this base granulation object PG for fabrication into the 100 weight sections, the above-mentioned press forming is performed so that the crack to the powder particle of the granulation [object / base granulation / PG / for fabrication] object PG at the time of a press may be promoted. An external surface side is processed by grinder cutting etc., and the appearance configuration corresponding to the insulator 2 of drawing 1 is made to Plastic solid 305, subsequently it is calcinated at the temperature of 1400-1600 degrees C, and turns into an insulator 2.

[0093] On the other hand, manufacture of a cover coat slurry is performed as follows. First, the source powder of a component used as each source of a component of Si, B, Zn, Ba, Na, and K for example, Si component -- SiO₂ powder and B component -- H₃BO₃ powder and Zn -- ZnO powder -- Ba component Na₂CO₃ powder and K for BaCO₃ powder and Na K₂CO₃ powder B component to B-2 O₃ 18 to 35% of the weight by the weight which carried out oxide conversion with the weight in which Si component carried out oxide conversion SiO₂ 25 - 40 % of the weight, While blending so that it may become 7 - 20 % of the weight ten to 25% of the weight by the weight which carried out the oxide conversion of the Ba at BaO with the weight which carried out the oxide conversion of the Zn component at ZnO About an addition alkali-metal component, by the weight in which carried out Na Na₂O and K carried out oxide conversion at K₂O, the above is blended three to 9% of the weight, and is mixed, respectively. Subsequently, melting of the mixture is heated and carried out to 1000-1500 degrees C, the melt is invested underwater, it vitrifies and a cover coat frit is made quenching and by grinding further. And proper quantity combination of a clay mineral and organic binders, such as a kaolin and frog clay, is carried out at this cover coat frit, and a cover coat slurry is obtained by adding water further and mixing.

[0094] And as shown in drawing 10 , by spraying and applying this cover coat slurry S on the required front face of spraying-nozzle N to the insulator 2, 2d [of cover coat slurry application layers as a cover coat powder deposit]' is formed, and this is dried.

[0095] Next, the outline of attachment by the center electrode 3 and the terminal metallic ornaments 13 to an insulator 2 in which 2d [of this cover coat slurry application layer]' was formed, and the formation process of a resistor 15 and the conductive glass-seal layers 16 and 17 is as follows. First, as shown in drawing 11 (a), after inserting a center electrode 3 in the part I part 6a to the breakthrough 6 of an insulator 2, it is filled up with the electrically-conductive-glass powder H as shown in (b). And as shown in (c), in a breakthrough 6, the precompression of the powder H inserted and filled up with the presser bar 28 is carried out, and the first electrically-conductive-glass powder layer 26 is formed. Subsequently, by being filled up with the raw material powder of a resistor constituent, carrying out a precompression similarly, being further filled up with electrically-conductive-glass powder, and performing a precompression, as shown in drawing 11 (d), in a breakthrough 6, the first electrically-conductive-glass powder layer 26, the resistor constituent powder layer 25, and the second electrically-conductive-glass powder layer 27 will be in the state where the laminating was carried out from a center-electrode 3 side (below).

[0096] And as shown in drawing 12 (a), the assembly PA which has arranged the terminal metallic ornaments 13 from the upper part is formed in a breakthrough 6. It inserts into a furnace in this state, and heats in predetermined temperature of 800-950 degrees C which is more than glass softening temperature, and after that, the terminal metallic ornaments 13 are pressed fit in shaft orientations from a center electrode 3 and an opposite side into a breakthrough 6, and each class 25-27 of a laminating state is pressed in shaft orientations. Thereby, as shown in this drawing (b), each class is compressed and sintered and turns into the conductive glass-seal layer 16, a resistor 15, and the conductive glass-seal layer 17, respectively (above, glass-seal process).

[0097] More here than the cover coat of the conventional lead silicate glass system, the softening

temperature is 600-700 degrees C by adopting the above-mentioned composition, and from the content of Na component and K component being set up comparatively more highly, the cover coat frit contained in 2d [of cover coat slurry application layers]' has a low softening temperature, and can carry out [low temperature]-izing of the glass firing temperature with 800-950 degrees C. Therefore, as shown in drawing 12, glass firing of 2d [of cover coat slurry application layers]' is simultaneously carried out by heating in the above-mentioned glass-seal process, and it becomes 2d of cover coat layers. Moreover, if a view is changed, since heating temperature of a glass-seal process is low-temperature-ized from conventional 900-1000 degrees C to 800-950 degrees C, it is hard coming to also generate the oxidization to a center electrode 3 or the front face of the terminal metallic ornaments 13. Moreover, since the difference of coefficient of linear expansion with the alumina system insulating material which constitutes an insulator 2 is comparatively small, a cracking crack etc. cannot produce the cover coat of the above-mentioned composition easily in 2d of cover coat layers at the time of cooling of the glass-seal process which served as this glass firing process.

[0098] In this way, to the assembly PA which the glass-seal process completed, the subject metallic ornaments 1 and grounding-electrode 4 grade are attached, and the spark plug 100 shown in drawing 1 is completed to it. A spark plug 100 is attached in a cylinder crank case in the thread part 7, and is used as an ignition source to the gaseous mixture supplied to a combustion chamber. Here, since it has added combining two kinds of alkali-metal components, Na and K, conductivity does not increase so much, but good insulation is secured, and the cover coat which constitutes 2d of cover coat layers is excellent in flashover-proof nature, although the content of an alkali-metal component is quite high as above-mentioned.

[0099] In addition, as shown not only in the thing of the type shown in drawing 1 but in drawing 5, the spark plug of this invention may make the nose of cam of a grounding electrode 4 counter with the side of a center electrode 3, and may form spark gap g among them. In this case, on both sides of a center electrode 3, as shown in drawing 6 (a), a grounding electrode 4 can also arrange 3 or the thing beyond it around a center electrode 3, as shown in this drawing (b) besides the mode 1 every each prepared a total of two. Moreover, as shown in drawing 7, you may constitute a spark plug 100 as a semi creeping-discharge type spark plug which made the point of an insulator 2 advance between the side of a center electrode 3, and the apical surface of a grounding electrode 4. With this composition, since spark discharge happens in the form where the front face of the point of an insulator 2 is met, corruption-proof nature improves compared with an aerial discharge type spark plug.

[0100] (Example 2) The example of the spark plug concerning the second composition of this invention is explained hereafter. The composition of the spark plug of this example 2 is completely the same as that of an example 1 except for composition of a cover coat layer, and the explanation about portions other than a cover coat layer uses drawing 1 - drawing 7 for, and omits the detailed explanation. 2d of cover coat layers consists of at least one sort as which the main cation component is chosen from Ti and Zr with Si, B, Zn, and Ba. B component to B-2 O3 20 to 40% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the Si component SiO2 20 - 35 % of the weight, While containing Ba component ten to 23% of the weight in BaO 15 to 25% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the Zn component at ZnO, Ti and Zr At least one sort which contains two to 10% of the weight in total by the weight in which carried out Ti TiO2 and Zr carried out oxide conversion ZrO2, respectively, and is chosen from Na, K, and Li is used as an alkali-metal component. Na -- Na2O and KK2 -- O and Li consist of cover coats which made the sum total content 12 or less % of the weight by the weight which carried out oxide conversion at Li2O, and made the content of Pb further 0.1 or less % of the weight in the form which carried out oxide conversion at PbO

[0101] Specifically, composition of the above-mentioned cover coat layer can be adjusted so that the thing of at least 1 of the following four modes may be satisfied. ** Make Si component into 20 - 38 % of the weight by the weight which carried out oxide conversion SiO2. ** Make ZrO2 equivalent-weight content of Zr into 3.4 or less % of the weight. ** Make TiO2 equivalent-weight content of Ti into 1.5 % of the weight or more. ** Set WTi/WZr to 0.2-10, using TiO2 equivalent-weight content of WZr and Ti as WTi for the ZrO2 equivalent-weight content of Zr.

[0102] It is only that raw material combination composition of the cover coat slurry which uses the process of the spark plug 100 which has the 2d of the above-mentioned cover coat layers differs, and others are the same as that of an example 1 almost. The source powder of a component with which manufacture of a cover coat slurry becomes Si, B, Zn and Ba, and at least one sort of each sources of a component chosen

from Ti and Zr for example, Si component -- SiO₂ powder and B component -- H₃BO₃ powder and Zn -- ZnO powder -- Ba component TiO₂ powder and Zr for BaCO₃ powder and Ti ZrO₂ powder B component to B-2 O₃ 20 to 40% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the Si component SiO₂ 20 - 35 % of the weight, While containing Ba component ten to 23% of the weight in BaO 15 to 25% of the weight by the weight which carried out oxide conversion with the weight which carried out the oxide conversion of the Zn component at ZnO, Ti and Zr It blends and mixes so that it may become what is contained two to 10% of the weight in total by the weight in which carried out Ti TiO₂ and Zr carried out oxide conversion ZrO₂, respectively. in addition, the case where at least one sort chosen from Na, K, and Li is blended as an alkali-metal component -- Na -- Na₂O and KK₂ -- O and Li blend the source powder of a component so that it may become 12 or less % of the weight about the sum total content by the weight which carried out oxide conversion at Li₂O Subsequently, melting of the mixture is heated and carried out to 1000-1500 degrees C, the melt is invested underwater, it vitrifies and a cover coat frit is made quenching and by grinding further. And proper quantity combination of a clay mineral and organic binders, such as a kaolin and frog clay, is carried out at this cover coat frit, and a cover coat slurry is obtained by adding water further and mixing.

[0103] By choosing the content range of the above alkali-metal components and B component, viscosity becomes possible [preparing easily the cover coat slurry which is small rich in a fluidity]. By spraying and applying this cover coat slurry S on the required front face of an insulator 2 from spraying-nozzle N, thickness is uniform and can form 2d [of glaze cover coat slurry application layers]' with little cellular contamination etc. so that drawing 10 may be used for and shown. Hereafter, since the process which obtains a spark plug from dryness through glost firing is the same as an example 1 almost, detailed explanation is omitted. By glost firing, thickness is uniform and 2d of cover coat layers with few defects can be obtained. Moreover, a cover coat softening temperature is as low as 600-700 degrees C, and since heating temperature of a glass-seal process is low-temperature-ized from conventional 900-1000 degrees C to 800-950 degrees C, it stops easily also being able to produce the oxidization to a center electrode 3 or the front face of the terminal metallic ornaments 13 as a result like an example 1. Furthermore, since the difference of coefficient of linear expansion with the alumina system insulating material which constitutes an insulator 2 is comparatively small, a cracking crack etc. cannot produce the cover coat of the above-mentioned composition easily in 2d of cover coat layers at the time of cooling of the glass-seal process which served as this glost firing process. On the other hand, since there are few contents of an alkali-metal component, good insulation is secured and the cover coat which constitutes 2d of cover coat layers is excellent in flashover-proof nature.

[0104] In addition, how to choose composition, as for the spark plug of the above-mentioned example 1 and an example 2 may become what has 2d of same cover coat layers. In this case, the effect in the first composition and the effect in the second composition can be attained simultaneously.

[0105]

[Example(s) of Experiment] The following experiments were conducted in order to check the effect of this invention.

(Example 1 of an experiment) The insulator 2 was produced as follows. First, it is alumina powder (95 % of the weight of aluminas, and 0.1 % of the weight (Na₂O reduced property) of Na contents) as raw material powder. As opposed to 3.0 micrometers of mean particle diameters SiO₂ (% [of purity / 99.5], 1.5 micrometers of mean particle diameters), CaCO₃ (99.9% of purity, 2.0 micrometers of mean particle diameters), MgO (99.5% of purity) 2 micrometers of mean particle diameters, and BaCO₃ (99.5% of purity, 1.5 micrometers of mean particle diameters) and H₃, while blending BO₃ (99.0% of purity, 1.5 micrometers of mean particle diameters), and ZnO (99.5% of purity, 2.0 micrometers of mean particle diameters) by the predetermined ratio The base slurry for fabrication was produced by adding 3 weight sections and the water 103 weight section, and carrying out wet blending of the PVA as a hydrophilic binder by making this blended powder total amount into the 100 weight sections.

[0106] Subsequently, the slurry from which these composition differs was dried by the spray-drying method, respectively, and the spherical base granulation object for fabrication was prepared. In addition, the particle size regulation of the granulation object is carried out to the particle size of 50-100 micrometers with the sieve. And it fabricated in pressure 50MPa by the rubber-press method which explained this granulation object using drawing 9, and while giving grinder grinding to the peripheral face of the Plastic solid and processing it in the shape of [predetermined] an insulating bodily shape, the insulator 2 was obtained by calcinating at the temperature of 1550 degrees C. In addition, it is 2O:aluminum component:aluminum₃ equivalent weight that the insulator 2 has the following composition turned out to

be by X-ray fluorescence, and is 94.9 % of the weight.;

Si component: It is SiO₂ equivalent weight and is 2.4 % of the weight.;

calcium component: It is CaO equivalent weight and is 1.9 % of the weight.;

Mg component: It is equivalent weight at MgO and is 0.1 % of the weight.;

Ba component: It is equivalent weight at BaO and is 0.4 % of the weight.;

B component: It is 0.3 % of the weight at B₂O₃ equivalent weight.

[0107] Moreover, :L1 whose each part size of the insulator 2 in which drawing 4 (a) is used for and shown is as follows = About 60mm, L -- 2 = about 8mm and L -- 3 = about 14mm and D -- 1 = about 10mm and D -- 2 = about 13mm and D -- 3 = about 7mm D 4= 5.5mm D 5= 4.5mm D 6= 4mm D 7= 2.6mm t 1= 1.5mm t 2= 1.45mm t 3= 1.25mm and tA=1.35mm Furthermore, when drawing 1 was used for and shown and the longitudinal section which the length LQ of partial 2k projected to the back side of the subject metallic ornaments 1 of an insulator 2 is 25mm, and contains the medial-axis line O of an insulator 2 is taken In the peripheral face of lobe part 2k of an insulator 2, length LP measured along with the **** visible outline until it reaches [from the position corresponding to the back end edge of the subject metallic ornaments 1] the back end edge of an insulator 2 through corrugation 2c is 29mm.

[0108] Next, the cover coat slurry was prepared as follows. As a raw material, first, SiO₂ (99.5% of purity), H₃BO₃ powder (98.5% of purity), ZnO powder (99.5% of purity), BaCO₃ powder (99.5% of purity), Na₂CO₃ powder (99.5% of purity), K₂CO₃ powder (99% of purity), 2Oaluminum₃ powder (99.5% of purity), 2OFe₃ powder (99.0% of purity), CaCO₃ powder (99.8% of purity), TiO₂ powder (99.5% of purity), SrCO₃ powder (99% of purity), SnO₂ powder (99% of purity), and FeO powder (99% of purity) are blended by various ratios. Melting of the mixture was heated and carried out to 1000-1500 degrees C, the melt was invested underwater, it vitrified and the cover coat frit was produced quenching and by grinding in particle size of 50 micrometers or less with the pot mill made from an alumina further. And 2 weight sections combination of the PVA as 3 weight sections and an organic binder was carried out for the New Zealand kaolin as a clay mineral to this cover coat frit 100 weight section, and the cover coat slurry was further obtained for water the 100 weight sections, in addition by mixing.

[0109] This cover coat slurry was dried after spraying on the front face of an insulator 2 from the spraying nozzle like drawing 10, and 2d [of cover coat slurry application layers] was formed. In addition, the application thickness of the cover coat after dryness is about 80 micrometers. Various creation of the spark plug 100 shown in drawing 1 was carried out by the method already explained using drawing 11 - drawing 12 using this insulator 2. However, the outer diameter of a thread part 7 was set to 14mm. Moreover, as raw material powder of a resistor 15, B-2O₃-SiO₂-BaO-Li₂O system glass, ZrO₂ powder, carbon black powder, TiO₂ powder, and metal aluminum powder were used, B-2O₃-SiO₂-Na₂O system glass, Cu powder, Fe powder, and Fe-B powder were used as raw material powder of the conductive glass-seal layers 16 and 17, respectively, and it performed at 900 degrees C, the heating temperature, i.e., the glost firing temperature, at the time of In addition, the thickness of 2d of cover coat layers formed in the front face of each insulator 2 was about 50 micrometers in general.

[0110] On the other hand, the cover coat sample made to solidify massive, without grinding was also produced. In addition, this massive cover coat sample checked vitrifying according to an X diffraction (amorphous-izing). The following experiment was conducted using this. ** Chemical-composition analysis : it is based on X-ray fluorescence. The analysis value (based on the value which carried out oxide conversion) for every sample is shown in Table 1 and 3. In addition, although each composition of 2d of cover coat layers formed in the front face of an insulator 2 was measured by the EPMA method, it has checked carrying out simultaneously coincidence with the analysis value measured using this massive sample. ** Coefficient of thermal expansion : the size 5mmx5mmx10mm measurement sample was started from the massive sample, and it has measured as the average from 20 degrees C to 350 degrees C by the well-known dilatometer. Moreover, when the measurement sample of the above-mentioned size was started also from the insulator 2 and same measurement was performed, the value was 73x10⁻⁷/degree C. ** Softening temperature : differential thermal analysis was performed heating 50mg of powder samples, and the temperature which carried out the measurement start and became the 2nd endothermic peak from the room temperature was measured as a softening temperature.

[0111] Moreover, about each spark plug, it carried out in energization voltage 1000V by the method which already explained the 500-degree C insulating resistance measurement using drawing 8. Moreover, the formation state of 2d of cover coat layers over an insulator 2 was observed visually. The above result is shown in Table 1 - 4.

[0116] That is, about the spark plug in which the cover coat layer with which are satisfied of the requirements for the composition of the first of this invention was formed, it turns out that the defect of a cracking crack and others does not arise in a cover coat layer, but the good cover coat layer is obtained also at the glost firing temperature of the low temperature which is 800-950 degrees C. Moreover, although there are many contents of an alkali-metal component, the insulation resistance of 500 degrees C is as high as 200 M omega or more, and having good flashover-proof nature is suggested.

[0117] (Example 2 of an experiment) The insulator 2 of the completely same configuration as the example 1 of an experiment and the quality of the material was prepared. Moreover, the cover coat slurry was prepared as follows. As a raw material, first, SiO₂ (99.5% of purity), H₃BO₃ powder (98.5% of purity), ZnO powder (99.5% of purity), BaCO₃ powder (99.5% of purity), Na₂CO₃ powder (99.5% of purity), K₂CO₃ powder (99% of purity), Li₂CO₃ powder (99% of purity), 2Oaluminum3 powder (99.5% of purity), CaCO₃ powder (99.8% of purity), TiO₂ powder (99.5% of purity), ZrO₂ powder (98% of purity) was blended by various ratios, melting of the mixture was heated and carried out to 1000-1500 degrees C, and the cover coat frit was produced by investing the melt underwater, and grinding to 9-10 micrometers of mean particle diameters with the pot mill made from an alumina further, after vitrifying, quenching and. And the cover coat slurry was obtained by blending and mixing the kaolin (British kaolin) as a clay mineral so that the remainder may serve as an acrylic organic binder 35% of the weight 1% of the weight 10% of the weight and may serve as the above-mentioned cover coat frit in water.

[0118] In order to stabilize the elution state of B component from a cover coat frit, and an alkali-metal component, each obtained slurry was measured using the Brookfield viscometer (form : B type, the Tokyo Keiki Co., Ltd. make, part number BH), after leaving it for ten days in a 40-degree C thermostat.

[0119] And except for the point using the above-mentioned cover coat slurry, others carried out various creation of the spark plug 100 shown in drawing 1 according to the same conditions as the example 1 of an experiment (1000 per cover coat composition). In addition, the thickness of 2d of cover coat layers formed in the front face of each insulator 2 was about 50 micrometers in general. In this way, about each obtained spark plug, the 500-degree C insulating resistance measurement was performed like the example 1. Moreover, the formation state of 2d of cover coat layers over an insulator 2 was observed visually.

[0120] On the other hand, the cover coat sample made to solidify massive, without grinding was also produced. In addition, this massive cover coat sample checked vitrifying according to an X diffraction (amorphous-izing). The following experiment was conducted using this.

**** Chemical-composition analysis :** it is based on X-ray fluorescence. The analysis value (based on the value which carried out oxide conversion) for every sample is shown in Table 5. In addition, although each composition of 2d of cover coat layers formed in the front face of an insulator 2 was measured by the EPMA method, it has checked carrying out simultaneously coincidence with the analysis value measured using this massive sample.

**** Softening temperature :** differential thermal analysis was performed heating 50mg of powder samples, and the temperature which carried out the measurement start and became the 2nd endothermic peak from the room temperature was measured as a softening temperature. The result is shown in Table 6.

**** It judged by viewing whether the cracking crack or the crazing would have occurred to the cover coat layer obtained by glost firing, and asked for the generating number in 1000 pieces. The result is shown in Table 6.**

[0123] That is, about the spark plug in which the cover coat layer with which are satisfied of the requirements for the composition of the second of this invention was formed, the melting state of a cover coat layer is good, and the generating frequency of a cracking crack or a crazing is also known by that it is small. The good cover coat layer is obtained especially again also at the glost firing temperature of 800-950-degree C low temperature. Moreover, the insulation resistance of 500 degrees C is as high as 200 M omega or more, and having good flashover-proof nature is suggested. Moreover, the cover coat slurry used for cover coat layer formation has comparatively small viscosity, it is homogeneous, and it turns out that it has contributed to few cover coat layer formation of a defect.